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Author(s): Rex P. Hjelm, Jarek Majewski LANSCE-12
Christopher J. Durning, K.M. Anis Rahman
Department of Chemical Engineering, Columbia Univeristy

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Rex P. Hjelm, Jarek Majewski LANSCE-12

Christopher J. Durning, K.M. Anis Rahman
Department of Chemical Engineering, Columbia University

Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). We developed competency in the use of neutron scattering in the study of shear-induced effects in polymers. Specifically, we studied shear-induced polymer associations in the bulk and polymer conformation and orientation at interfaces using small-angle neutron scattering and neutron reflectometry, respectively. The issues are fundamental to understanding shear effects in industrial processing of polymers, and they are of importance to the physics of polymer fluids. We looked at the character of the surface and the polymers in promoting or reducing slippage and orientation. We built two devices for the simultaneous measurements of structure and rheological properties of polymers, allowing correlation of the two.

Background and Research Objectives

Our objective was to develop competency in the use of neutron scattering for the study of shear-induced effects in polymers. We used small-angle neutron scattering (SANS) and neutron reflectometry (NR) to study shear-induced polymer associations, conformation and orientation in the bulk and at interfaces. Specifically, we studied shear-induced polymer associations and shear slippage of polymers at interfaces. These phenomena are fundamental to understanding shear effects in the industrial processing of polymers, and they are also of importance to the physics of polymer fluids. We built two devices to simultaneously measure structure and rheological properties of polymers in order to correlate the properties.

Shear is introduced in industrial processing when a polymer melt or concentrated solution is passed through an orifice, such as a spinner, used in fiber formation, or by injection into a mold. Thus, the effects of shear on polymer conformation, surface interactions and orientation are of considerable industrial interest.

*Principal Investigator, e-mail: hjelm@lanl.gov

There has been substantial effort attempting to uncover the physics underlying the behavior of polymers under shear. However, a detailed understanding that could be used to connect the structure of polymers with their unique rheological properties has yet to emerge. Thus, there is little basis on which to make predictions on the effect of an industrial processing strategy on the material properties, and hence the characteristics, of the final product.

Polymers used in industrial applications form an extensive list. Examples include nylon, polyolefins and polystyrene. In these systems the high speed of injection in practical molding applications leads to polymer slippage at the surface. The main consequence of this is poor product appearance and surface distortions, though more severe manifestations of the underlying non-Newtonian behavior include flow instabilities leading to internal inhomogeneities that can affect the durability of the product. Other polymer systems used in applications are soluble, micelle-forming polymers, such as pluronic triblock copolymers, widely used as polymer surfactants. These polymers show interesting shear-induced aggregation behavior that relates to their applications.

Importance to LANL's Science and Technology Base and National R&D Needs

This basic research seeks to improve our understanding of the molecular basis of polymer materials properties and behavior and how to make materials perform better at acceptable cost through new methods of synthesis and processing in the areas of polymers and their composites. In particular, the work is in surface science and in the development of new approaches and instrumentation for the non-destructive evaluation of surface properties using the unique capabilities of neutron scattering and reflectometry. The connection to the Laboratory core competencies are in the development of the facilities at the Los Alamos Neutron Science Center (LANSCE) to approach a significant new area of research in materials science and its relationship to the industrial end uses of polymers in general. Our research addressed directly the Laboratory's tactical goals in Industrial Partnerships. This competency developed in this project also benefits indirectly the programs in Science Based Stockpile Stewardship.

The information gained from this work has broad impact in understanding the inherent stability of structural fluids. Increased understanding of more complex systems, such as polymer blends and multiphase fluids, can be approached by first understanding the nature of the polymer-polymer and polymer-wall interactions under shear stress.

Scientific Approach and Accomplishments

Both SANS and NR probe length scales where polymer conformation and orientation are readily visualized. Neutrons have high penetrability for polymers and the materials used in the shear apparatus (as opposed to x-rays). There are well-developed methods for the synthesis of deuterated polymers to provide contrast between interface polymers and bulk polymers or between the polymers and the bulk solvent that cannot be contrasted by other methods. Thus, the neutron methods provide molecular level information on systems under shear that is unique and not available directly by other techniques.

Response to Steady Shear Stress in the Bulk— SANS Measurements

To study shear effect in the bulk, we built a Couette-geometry rheometer for SANS (Figure 1). The unit, fabricated from aluminum and containing heating elements in the core and thermostat enclosure, was designed to study melts in the temperature range of ambient to 200 °C. The combined capabilities of this unit and another made of fused silica with an Invar core that can be temperature-controlled using a circulating water bath, extends the temperature range down to about -20 °C.

We used the fused-silica fluid-thermostated cell to study the effects of shear on the temperature-dependent aggregation of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers. These polymers, which are available commercially in a number of molecular weights and compositions, are soluble at solution concentrations up to 33 weight percent at low temperatures and form micelles or gels at higher temperatures. As the temperature increases spherical micelles then rods are formed.^{1,2} The micelles consist of a PPO core surrounded by a heavily solvated PEO corona. There are interesting rheological behaviors associated with the phase map of these polymers.³ There is little work in the area of shear-induced association effects in micelle-forming polymers and the intermolecular interactions at lower concentrations. Neutron scattering can provide essential base data on the factors that enhance or reduce this effect.

In our studies we looked at the shear- and temperature-induced structure of PEO₁₇-PPO₆₀-PEO₁₇. At 19 °C and 33 °C this material forms strongly spherical micelles. The interaction increases with temperature. With the application of shear at 19 °C and 33 °C the interaction is lowered to the point that the scattering at 19 °C is characteristic of weakly interacting micelles at a shear rate, $\dot{\gamma}$, of 1.0 Hz (Figure 2A). There are no orientation effects at 19 °C and 33 °C. At 38 °C there are strong orientation effects of the rods (Figure 2B). Further analysis of the data is needed to understand how the interactions are affected by shear, and how this relates to the interesting rheological behavior of these materials.

Response to Steady Shear at Interfaces—Neutron Reflectometer Measurements

It is known that there are particularly strong effects near the surface of a processing device in polymer melts at moderate shear rates. These effects are due largely to the constraints imposed on the polymer chains at the surface, which are distinct from the bulk material. The characterization of these effects and the temperature, molecular weight and shear rate dependence is important in connecting these phenomenon with the macroscopic rheological behavior.

Anomalous fluid behavior near a pipe wall was first recognized some fifty years ago.⁴ This behavior, the slip effect, can be described by an extrapolation length, b , which is the point beyond the wall at which the flow velocity would be equal to zero. There have been various reports on wall slip phenomenon.⁵⁻⁷ However, the full chain dynamics during the slip induction remains unknown.

In wall slippage the nature of the polymer and its interaction with the surface play critical and fundamental roles. In the case of shear slip, interactions of the polymer next to the surface are expected to be distinct from the bulk and the behavior of interface layer is determined by its interactions with the surface on the one hand, and the adjacent polymer layers on the other. For example, a plausible picture of slippage of coiled polymers indicates the importance of surface effects in these systems. At low strain rate the polymer layer at the wall surface will have several direct contacts with the surface and loops and tails entangled with the bulk polymer medium. At high shear there may be a loss of a number of contacts inducing adhesive fracture at the interface. Alternatively (or perhaps concomitantly), the shear stress is non-uniform between the bulk and interface polymer layer, and the polymer chains at the wall surface become so highly oriented that entanglements are lost and the intermolecular forces present are only a result of chain - chain sliding. The problem of polymer slippage at a wall is to define the shear-induced conformation near the surface that leads to slippage based on the extrapolation length associated with slip.

According to deGennes⁸, the extrapolation length should vary with molecular weight as:

$$b = \frac{\eta_1}{k} N^m \quad [1]$$

where N is the number of monomers per chain, and the exponent m has a value near 3. Higher molecular weight provides more entanglements per chain and directly decreases the

probability of cohesive slip. Eq. [1] and similar predictions imply that slip-shear be studied as a function of interface and bulk polymer molecular weight, temperature, substrate interactions and shear rate.

A flat plate shear cell with cone-and-plate geometry was built for these studies (Figure 3). This device was equipped with a precision servomotor, allowing high accuracy over a broad range of rotational speeds. Both steady shear and dynamic motion profiles are programmable. The controller is equipped with a signal feedback, which allowed the operation of the scattering cell in a constant-stress mode and the determination of the sample viscosity. The upper, stationary plate could be made from fused silica, single-crystal quartz or single-crystal silicon. The plates served as substrates for the interface polymers. All three were used in different experiments. The lower, rotating cone holds the bulk sample. The bulk sample is usually polymer melt. The entire cone-and-plate assembly is placed in a furnace, providing an environment from ambient temperature to about 190 °C, allowing us to study a number of important polymer systems. Using this apparatus the wall slip phenomena can therefore be readily investigated as a function of the applied shear stress and correlated with changes in the near surface conformation of the polymer.

We performed preliminary NR measurements at the National Institute of Standards and Technology, Gaithersburg, MD. One goal of our project is to study the behavior of polymer brushes of polystyrene bound to a substrate against a melt of polystyrene. In order to distinguish between the bound polystyrene and the melt, the melt is deuterated. We spin coated a 198-KDa PMMA/117-KDa polystyrene block copolymer onto a quartz substrate. This was then over-layered with 143-KDa deuterated polystyrene. The procedure produced a polymer “brush” on the quartz as shown by the NR data in Figure 4. PMMA, which was immiscible with the polystyrene, anchored the brush to the fused quartz. The polystyrene block then extended from this anchor and made contact with the layer of deuterated polystyrene. The freshly coated and dried sample showed a reflectivity pattern characteristic of a relatively sharp interface between the polystyrene and the deuterated over-layer at about 220 Å from the fused quartz surface (Figure 4). After annealing the sample showed a more diffuse boundary (Figure 4).

Our first shear experiments were done on the surface structure of high- and low-density polystyrene brushes next to polystyrene melts as a function of shear rate. (Brushes are linear polymer molecules attached to the plate at one end; melts are polymers heated to become a fluid.) In this experiment a single-crystal silicon wafer, used as the upper plate in the rheometer, was used as the substrate. Deuterated, monodisperse, 80-KDa polystyrene was

grafted to the silicon surface in two densities, the denser of the two being termed a “full” brush as opposed to the less dense “partial” brush. The bulk sample consisted of hydrogenated, 282-KDa polystyrene with 30% by weight dioctylphthalate. We estimated the thickness of the brushes to be 50 Å and 84 Å, respectively, for the partial and full brushes using x-ray reflectometry.

Figure 5 exhibits the normalized specular reflectivity data of the “full-brush” samples. The top curve corresponds to the reflectivity of dry brush in air. The presence of a well-defined fringe pattern indicates that the dry full-brush layer resembles a homogeneous, amorphous, thin polymer layer. Figure 5 also shows the reflectivity data of the full-brush layer in contact with the melt at 145 °C without shear and with shear. The reflectivity spectra corresponding to the brush in contact with the melt shows that the sharp layer definition of the dry brush is lost due to wetting by the melt, as indicated by the absence of the well-defined fringes and shifting down of the spectrum.⁹⁻¹¹ Under a small shear (0.0002 Hz), the brush exhibits a small increase in the reflectivity compared to the non-shear case. This perhaps is due to tilting and/or slight elongation of the brushes¹²; however, a systematic modeling is under way to probe further the nature of this change.

Publication

1. Hjelm, R.P., “The Structure of Fillers, Polymers and Their Interfaces in Polymer Composites using Neutron Scattering Methods,” *Proceedings of the 153rd Meeting of the American Chemical Society Rubber Division, Indianapolis* (ACS Polymer Rubber Division, Akron, Ohio, 1998), Vol. 153, p. 8.

References

- [1] Mortensen, K and Talmon Y., “Cryo-TEM and SANS Microstructural Study of Pluronic Polymer Solutions” *Macromolecules*, **28**, 8829-8834 (1995).
- [2] Glatter, O., Scherf, G., Schillén, K and Brown, W., “Characterization of a Poly(ethylene oxide)-Poly(propylene oxide) Triblock Copolymer (EO₂₇-PO₃₉-EO₂₇) in Aqueous Solution”, *Macromolecules*, **27**, 6046-6054 (1996).
- [3] Prud’homme, R.K., Wu, G., Schneider, D.K., “Structure and Rheology Studies of Poly(oxyethylene-poxypropylene-oxyethylene) Aqueous Solution”, *Langmuir*, **12**, 4651-4659 (1996)
- [4] J.G. Oldroyd, *J. Colloid Sci.*, **4**, 333 1949.
- [5] J.M. Dealy and S.G. Hatzikiriakos, *J. Rheol.*, **36(5)**, 845 1992.

- [6] S-Q Wang and Y Inn, *Rheol Acta.*, **34(2)**, 108 1994.
- [7] K.B. Migler, H. Hervet and L. Leger, *Phys Rev. Lett.*, **70(3)**, 287 1993.
K.B. Migler et. al., *J. Phys.: Cond. Matter*, **6**, A301 1994.
- [8] P.G. de Gennes, *C. R. Acad. Sci B*, **288**, 219 1979.
- [9] T. P. Russell, "X-ray and neutron reflectivity for the investigation of polymers," *Matl. Sci. Rep.*, **5** (4,5), 1990, 171-271.
- [10] G.J. Fleer, M.A. Cohen Stuart, J.M.H.M. Scheutjens, T. Cosgrove and B. Vincent, "Polymers at Interfaces," Chapman & Hall, New York: 1993.
- [11] F.T Kiff, R.W. Richards, H.L. Thompson, D.G. Bucknell and J.R.P. Webster, "Influence of matrix molecular weight on a brush – like surface layer formed by a polymer functionalized at both ends," *J. Phys. II France*, **7**, 1997, 1871-1891.
- [12] L. Miao, H. Guo and M.J. Zuckermann, "Conformation of polymer brushes under shear: chain tilting and stretching," *Macromolecules*, **29**, 1996, 2289-2297.

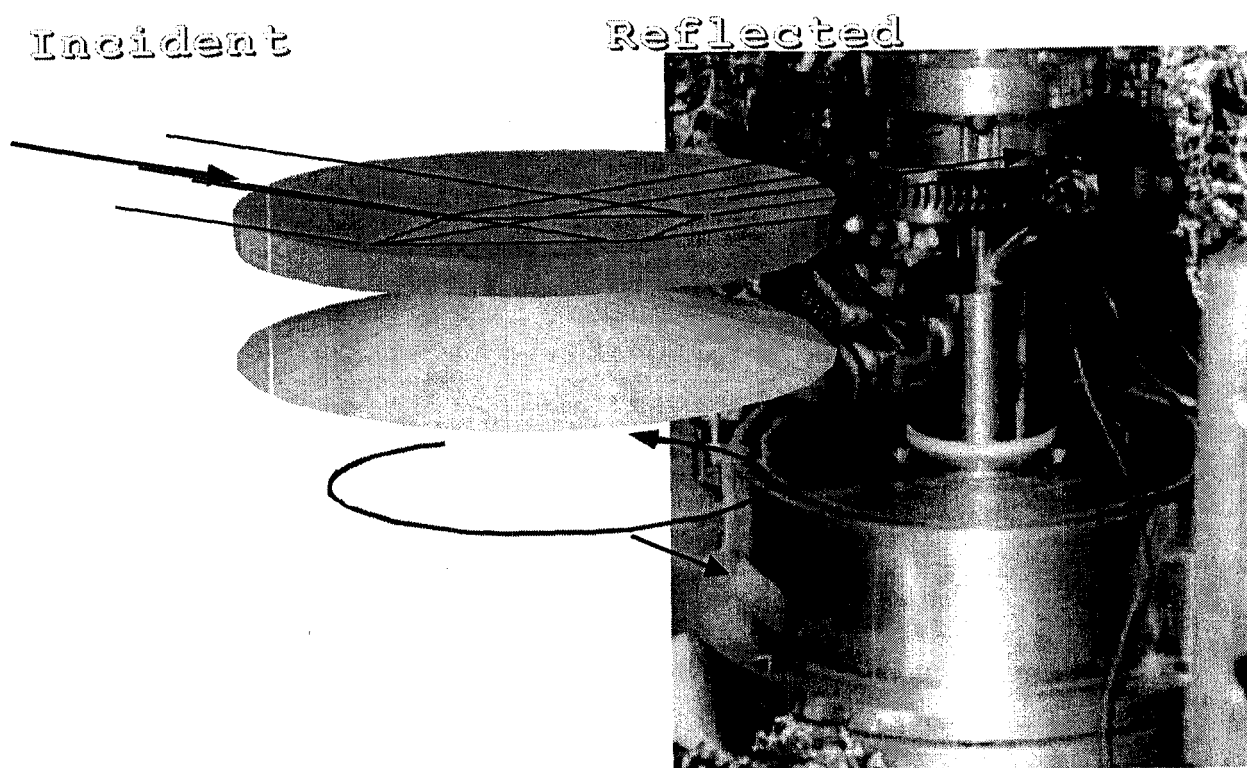


Figure 1. Couette-geometry rheometer SANS cell. Left is the schematic of the placement of the cell in the beam. Right is a picture of the aluminum, high temperature cell. Left to right is shown the thermostated core, rheometer bob and rotating cylinder. A similar assembly with a thermostated, fluid-cooled, Invar core and fused silica bob and cylinder is used for low temperature work.

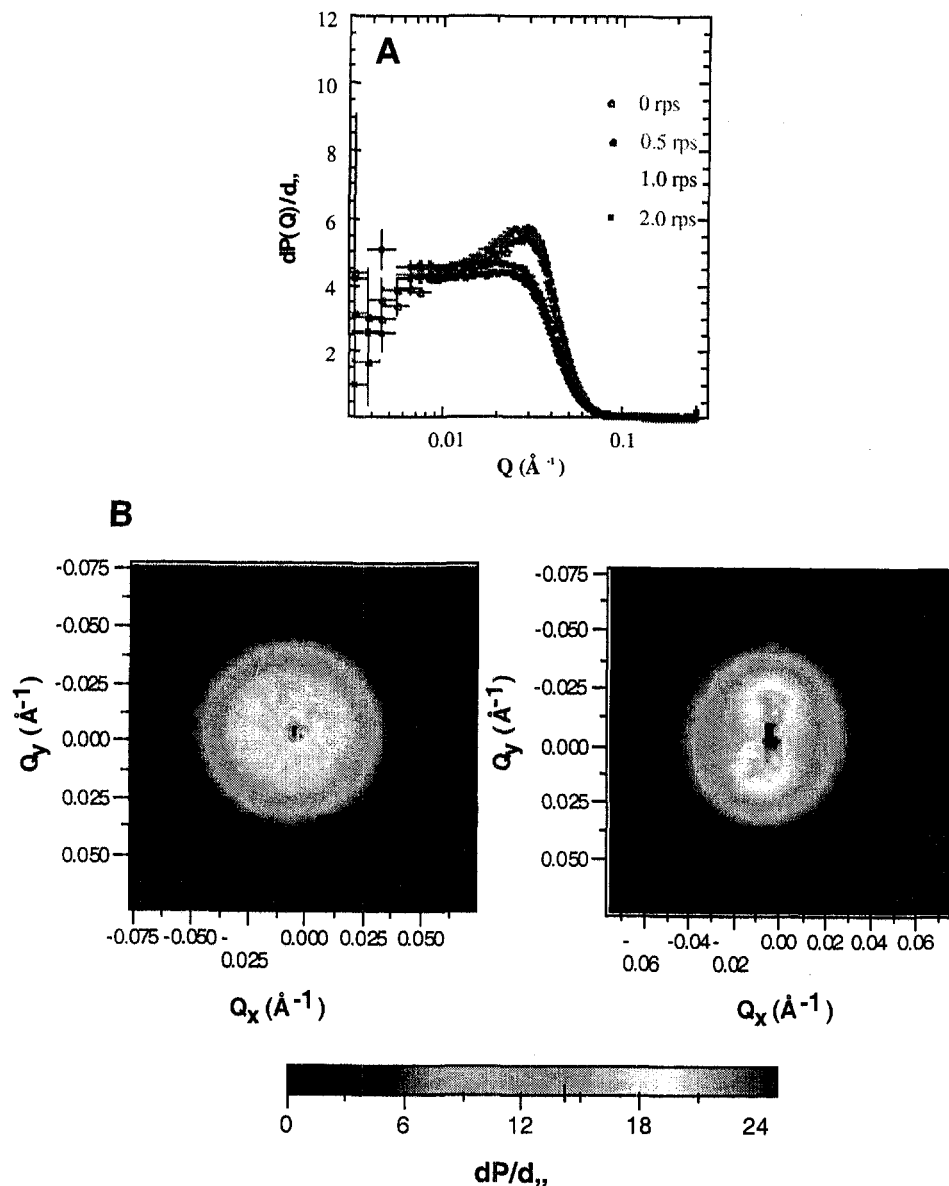
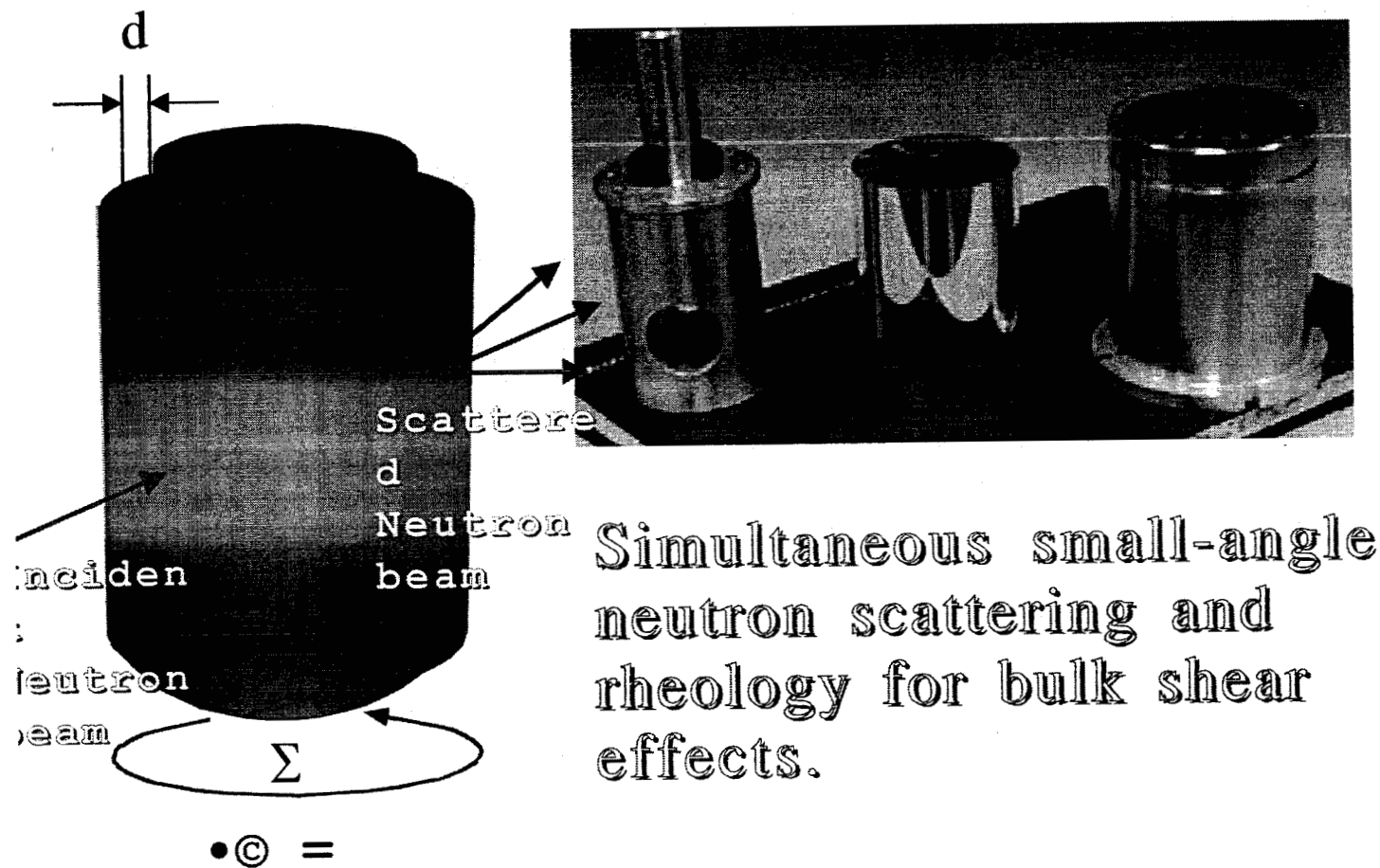


Figure 2. Shear effects on temperature-dependent micelle formation of $\text{PEO}_{17}\text{-PPO}_{60}\text{-PEO}_{17}$. (A) Radial-averaged neutron scatter at 19 °C at shear rates $\gamma \dot{\omega} = 0$ to 10 Hz. The peak observed in the sample at 0 and 0.5 Hz is indicative of micelle interactions. The loss of this peak at 1.0 and 2.0 Hz indicates the shear-induced breakup of these interactions. (B) A two-dimensional plot of the scattering from a sample at 38 °C. The isotropic scattering at $\gamma \dot{\omega} = 0 \text{ Hz}$ (left) is due to the random orientation of rods. The "butterfly" pattern present at $\gamma \dot{\omega} = 10 \text{ Hz}$ (right) indicates strong orientation of the rods.

Couette Shear Cell for SANS

96604



Simultaneous small-angle neutron scattering and rheology for bulk shear effects.

Figure 3. Cone-and-plate rheometer for neutron reflection studies of surface effects in polymers under shear. (Left) Schematic of the rheometer's stationary upper plate and rotating lower cone. The polymer brush is attached to the lower surface of the plate and the polymer melt is between the cone and polymer brush-coated plate. Neutrons are reflected from the interface between the brush and the melt and probe the structure of the interface. (Right) View of the rheometer that shows the furnace (flat cylinder at bottom) that contains the cone-and-plate assembly. Neutrons enter the oven through the oblong aluminum window on the left (arrow).

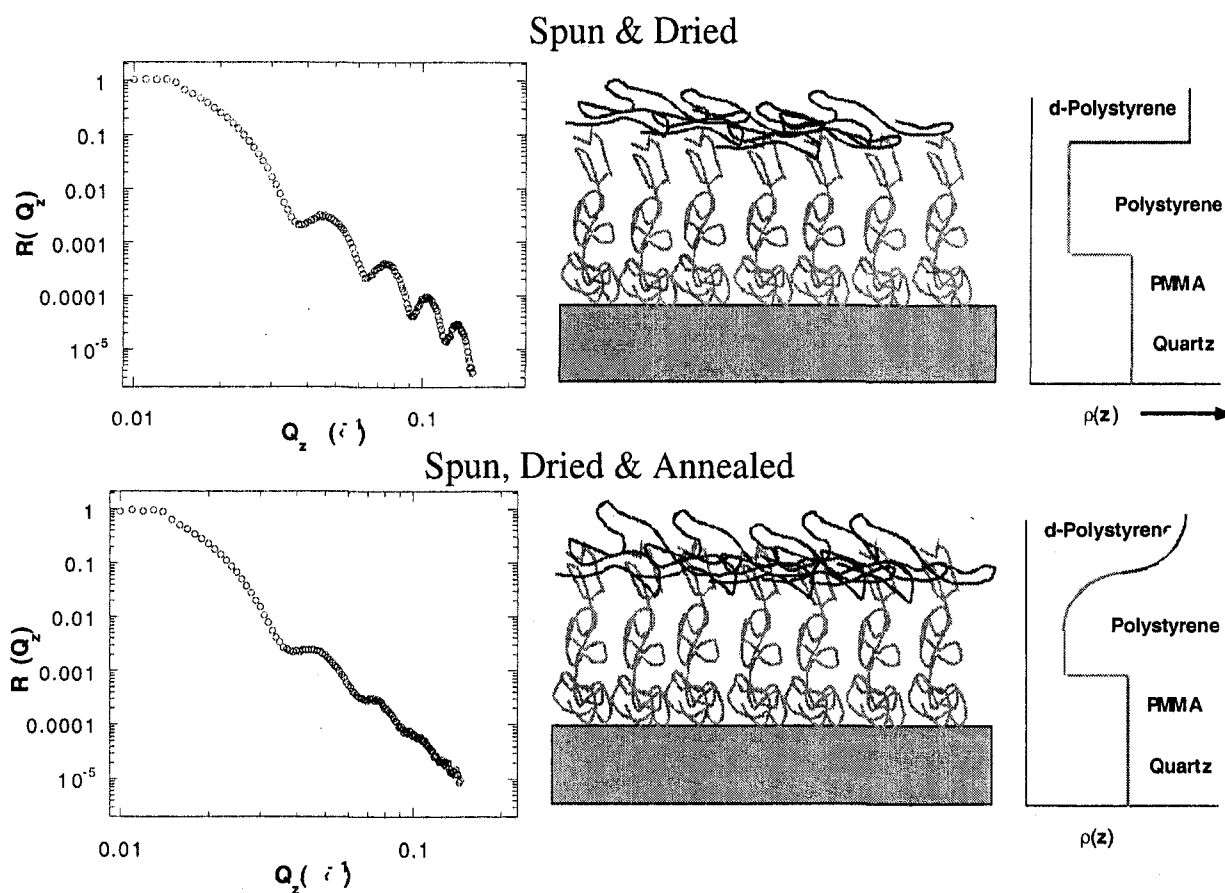


Figure 4. Neutron reflectometry of deuterated polystyrene on PMMA-polystyrene block copolymer brush, freshly dried and annealed. A 198-KDa PMMA/ 117-KDa polystyrene block copolymer is spun-cast on fused quartz. Deuterated 143-KDa polystyrene is overlaid. The freshly dried sample showed sharp fringes characteristic of distinct boundaries. The annealed sample showed reflectivity characteristic of interpenetrating boundaries.

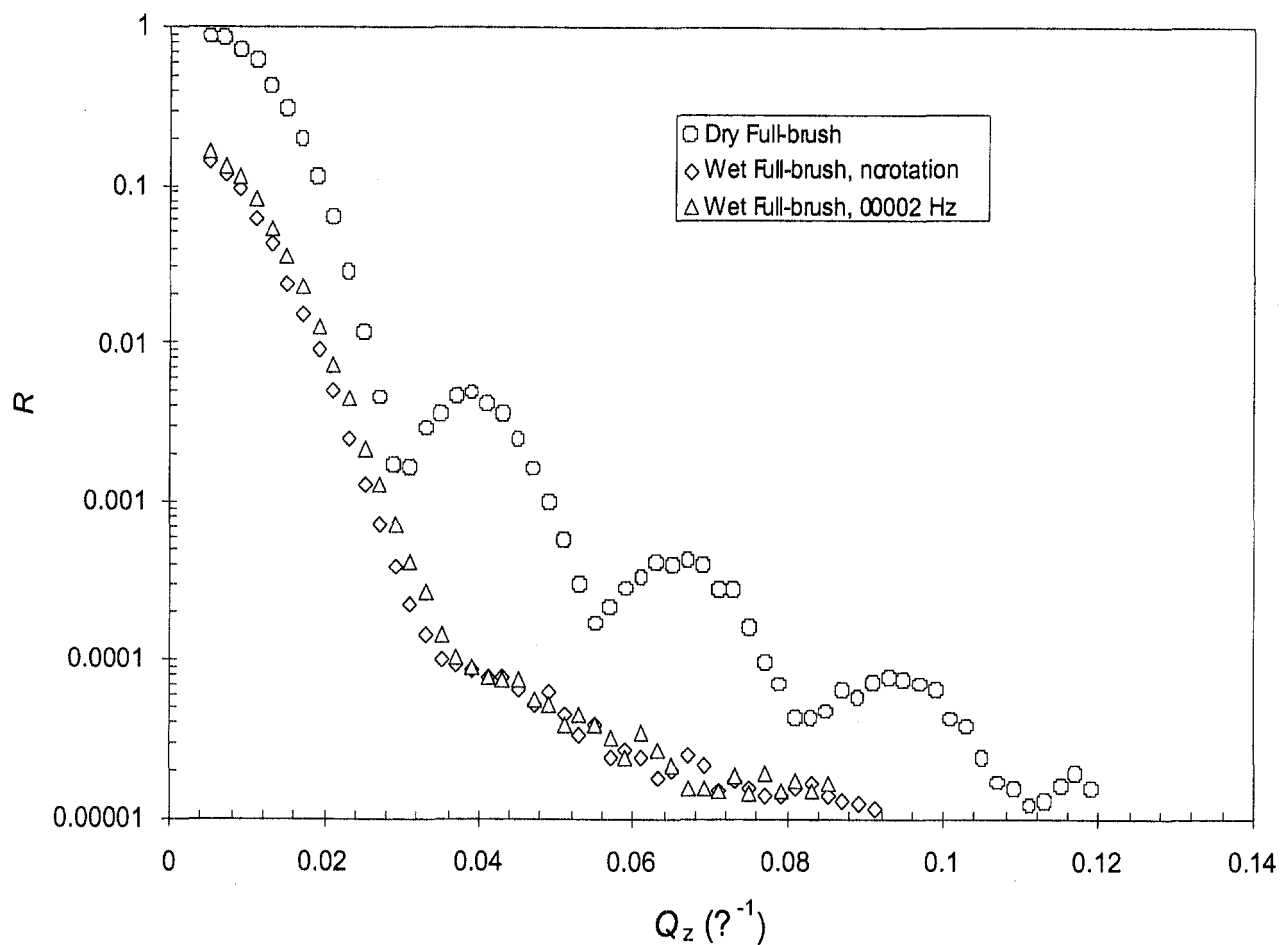


Figure 5. Normalized reflectivity of full brush including dry brush in air (circles), in contact with the melt at 145 °C (diamonds), and in melt with a shear rate of 0.0002 Hz (triangles).